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Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest

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Abstract. As a part of EUCAARI activities, the annual cycle of cloud condensation nuclei (CCN) concentrations and critical diameter for cloud droplet activation as a function of supersaturation were measured using a CCN counter and a HTDMA (hygroscopicity tandem differential mobility analyzer) at SMEAR II station, Hyytiälä, Finland. The critical diameters for CCN activation were estimated from (i) the measured CCN concentration and particle size distribution data, and (ii) the hygroscopic growth factors by applying κ -Köhler theory, in both cases assuming an internally mixed aerosol. The critical diameters derived by these two methods were in good agreement with each other. The effect of new particle formation on the diurnal variation of CCN concentration and critical diameters was studied. New particle formation was observed to increase the CCN concentrations by 70–110 %, depending on the supersaturation level. The average value for the κ -parameter determined from hygroscopicity measurements was $\kappa = 0.18$ and it predicted well the CCN activation in boreal forest conditions in Hyytiälä. The derived critical diameters and κ -parameter confirm earlier findings with other methods, that aerosol particles at CCN sizes in Hyytiälä are mostly organic, but contain also more hygroscopic, probably inorganic salts like ammonium sulphate, making the particles more CCN active than pure secondary organic aerosol.

1 Introduction

Atmospheric aerosol particles influence clouds, and thereby climate, by altering the albedo, lifetime and precipitation patterns of clouds (e.g. Twomey, 1974; Lohmann and Feichter, 2005; Rosenfeld et al., 2008; Stevens and Feingold, 2009). While aerosol-cloud interactions depend on a number of environmental factors, the primary aerosol-related quantity in this respect is the cloud condensation nuclei (CCN) concentration or, more specifically, the CCN supersaturation spectrum (Andreae and Rosenfeld, 2008).

During the last decade or so, CCN number concentrations and spectra have been measured in a variety of different environments (e.g. Snider and Brenguier, 2000; Bigg and Leck, 2001; Hudson and Yum, 2002; Roberts et al., 2006; Hudson and Noble, 2009). Another class of investigations, that has gained a large interest, is so-called CCN closure studies (e.g. Covert et al., 1998; Rissler et al., 2004; Broekhuizen et al., 2006; Ervens et al., 2007; Medina et al., 2007; Duplissy et al., 2008; Good et al., 2010; Poulain et al., 2010; Fors et al., 2011). In the closure studies, the measured CCN concentrations are compared with those obtained from equilibrium model calculations based on measured aerosol properties, such as the aerosol size distribution and chemical composition or hygroscopicity.

Determining the relative role of humans and nature in aerosol-cloud interaction requires identifying and quantifying different CCN sources. In addition to primary natural and anthropogenic sources, increasing empirical evidence has been obtained on secondary CCN production in the atmosphere via nucleation and growth of new aerosol particles (Lihavainen et al., 2003; Laaksonen et al., 2005;



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Kuwata et al., 2008; Kuang et al., 2009; Wiedensohler et al., 2009). Recent model studies indicate that secondary production may be an important CCN source in the global atmosphere (Spracklen et al., 2008a; Makkonen et al., 2009; Wang and Penner, 2009; Kazil et al., 2010; Yu, 2011), even though uncertainties in the overall magnitude of this source are still quite large (Pierce and Adams, 2009).

Boreal forests constitute one of the largest and most active areas of atmospheric new particle formation (Kulmala et al., 2001; Tunved et al., 2006; Dal Maso et al., 2007, 2008). While the potential of particles nucleated in boreal forests to act as CCN has been identified already some time ago (Lihavainen et al., 2003; Kerminen et al., 2005), direct CCN measurements in this environment have been extremely rare (Aalto and Kulmala, 2000; Hämeri et al., 2001). Such measurements would be of great help when studying aerosol-cloud interactions over boreal forests and, especially, when attempting to narrow down the uncertainties in indirect radiative effects due to boreal forest aerosols (Kurten et al., 2003; Spracklen et al., 2008b; Lihavainen et al., 2009).

In this paper, we present an analysis of simultaneous measurements of CCN concentrations, aerosol number size distributions and hygroscopic properties at a boreal forest site. We aim to shed light on the following questions: (i) what are the seasonal and diurnal variations of the CCN concentrations, corresponding activated fractions and critical diameters, (ii) how are the CCN concentrations affected by atmospheric new particle formation events, and (iii) can we predict the CCN activity of boreal forest aerosols based on measured aerosol size distributions and hygroscopic properties. Our analysis relies on one year of continuous measurements (July 2008–June 2009) conducted at the SMEAR II station in Hyytiälä, Finland.

2 Experimental

The SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations) station is located in a rather homogeneous Scots pine (*Pinus sylvestris* L.) stand on a flat terrain at Hyytiälä Forestry Field Station (61°51' N, 24°17' E, 181 m above sea level) of the University of Helsinki, 220 km north from Helsinki. The station represents boreal coniferous forest, which cover 8 % of the earth's surface and store about 10 % of the total carbon in terrestrial ecosystem. The biggest city near the SMEAR II station is Tampere, which is about 60 km south-west from the measurement site with about 200 000 inhabitants. Kulmala et al. (2001) and Hari and Kulmala (2005) have described the station and its operation in detail.

2.1 Cloud condensation nuclei (CCN) concentrations

Cloud condensation nuclei concentrations (N_{CCN}) were measured with a commercial diffusion-type CCN counter

(CCNC, Droplet Measurements Technologies inc., Roberts and Nenes, 2005). The CCNC consists of a saturator unit which mimics the supersaturated conditions inside a cloud. The sample flow, surrounded by a sheath flow (1/10 flow ratio), is led through the saturator unit, which is a vertical column with walls wetted by water. Inner walls of the column are covered with a porous material in order to maintain constant wetting. The sheath flow is humidified by using a Nafion-humidifier. The column temperature increases along the flow, generating a stable supersaturation along the centre-line. Particles that have a critical saturation ratio smaller than the peak saturation ratio will activate and grow to droplets by condensation. After the saturator, the droplets are counted by an optical particle counter (OPC). The OPC is heated to a temperature 2 °C higher than the bottom column temperature in order to avoid condensation of water vapour to the optics. The concentration of cloud condensation nuclei is thus obtained as a function of the water supersaturation ($SS = S - 1$, where S is saturation ratio). Supersaturations of 0.1, 0.2, 0.4, 0.6 and 1.0 % were used by selecting the corresponding temperature difference between the upper and bottom part of the saturator column.

The CCN counter was calibrated with ammonium sulphate particles, which were produced using an atomizer (TOPAS ATM 220). The size of the particle was selected with a differential mobility analyzer (DMA). A condensation particle counter (CPC, model TSI 3772) was used to count all the particles (N_{CN}) entering the CCNC. Calibrations were performed by keeping the temperature difference constant and varying the size of the ammonium sulphate particles entering the CCNC. The CCNC concentration was compared to the CPC concentration in order to define the critical diameter ($N_{\text{CCN}} / N_{\text{CN}} = 50 \%$) for each temperature difference, i.e. for each supersaturation. From this data the peak saturation ratio inside the column can be calculated by using Köhler theory. We utilized AP3-model, see Rose et al. (2008) for details. No size-selection was used during the ambient measurements.

2.2 Hygroscopicity measurements

A Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA, Liu et al., 1978; Ehn et al., 2007; Swietlicki et al., 1999, 2008) was used to measure the hygroscopicity of aerosol particles. In this instrument, the sample aerosol is first brought through a drier and a radioactive charger in order to reach a charge equilibrium and a relative humidity (RH) below 20 %. After this, a certain dry particle size, d_{dry} , is selected using a DMA. Next the particles are passed through a humidifier so that a certain controlled relative humidity is reached. Finally the humidified aerosol passes through another DMA which scanned the resulting humidified size distribution. The second DMA was located in a temperature-controlled box, maintained at a temperature of 19 ± 0.5 °C and relative humidity of 90 ± 1.5 %. Four dry sizes (110 nm, 75 nm, 50 nm and 35 nm), which belong to the standard sizes

agreed inside the EUCAARI project (Kulmala et al., 2009), were used.

2.3 Aerosol number size distribution

The total aerosol particle size distribution was measured using a differential mobility particle sizer (DMPS) in a size range from 3 nm to 1 μm . (Aalto et al., 2001). The aerosol sample is first dried to a RH < 30 %, after which the particles are charged using a radioactive bipolar charger. Then the particles are classified according to their (mobility) size using two separate DMAs for different size ranges (Twin-DMPS). The particle concentration after the DMA, corresponding to a certain particle size range, is measured with condensation particle counters (CPC, TSI 3025 for small (3–40 nm) particles and TSI 3010 for larger (15–1000 nm) particles).

3 Theoretical framework

3.1 CCN activation

The water uptake of an aerosol particle can be described by the Köhler equation (Köhler, 1936):

$$S = a_w \exp\left(\frac{4M_w\sigma}{RT\rho d_{\text{wet}}}\right), \quad (1)$$

where S is the water saturation ratio, a_w is the water activity, M_w is the molar mass of water, σ is the surface tension of the solution, R is the universal gas constant, T is temperature, ρ is the density of the solution and d_{wet} is the diameter of the wet particle. This equation connects the particle properties (size, surface tension, density and water activity) with the thermodynamic state of the surroundings (temperature, saturation ratio).

The measured total CCN concentrations (N_{CCN}) were compared to the aerosol size distribution data obtained from the DMPS measurements in order to estimate the activated fraction and the critical diameter from the ambient data. The activated fraction (F_{act}) for a certain supersaturation is defined here as:

$$F_{\text{act}}(S) = \frac{N_{\text{CCN}}(S)}{N_{\text{CN}}}, \quad (2)$$

where N_{CN} is the total concentration of the condensation nuclei obtained from the DMPS data.

The DMPS data can also be used to estimate the critical (dry) particle diameter for all the supersaturations used. In order to obtain this, the activation probability as a function of the particle size is assumed to behave like a step function, with all particles above the critical size (d_{crit}) activating. The particle size distribution is summed from the largest particle size towards the smaller sizes until the measured value of the CCN concentration is obtained. At that size the diameter corresponds to the critical diameter:

$$\sum_{d_p=d_{\text{crit}}}^{d_{\text{max}}} N_i = N_{\text{CCN}}. \quad (3)$$

This method includes the assumption that the aerosol is completely internally mixed, and this assumption will be discussed later in Sect. 4.2.2. The inverted aerosol number size distribution was represented by 38 size bins from 3 to 1000 nm (Aalto et al., 2001). In order to increase the resolution of the critical diameter estimate, a linear interpolation was used between each size bin of the DMPS.

3.2 HTDMA methods

In the simplest form, the hygroscopicity of a certain sized dry particle can be described as a growth factor

$$g_d = \frac{d_{\text{wet}}}{d_{\text{dry}}}, \quad (4)$$

where d_{wet} is the mean diameter of the humidified size distribution at a certain RH for the selected dry particle size d_{dry} .

The critical particle diameter for CCN activation at a certain supersaturation can be calculated also from the HTDMA data using the so called κ -Köhler equation (Petters and Kreidenweis, 2007) (see Eq. 1 for the notation)

$$S = \frac{d_{\text{wet}}^3 - d_{\text{dry}}^3}{d_{\text{wet}}^3 - d_{\text{dry}}^3(1 - \kappa)} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w d_{\text{wet}}}\right). \quad (5)$$

In this theory the Köhler equation is modified so that all the physico-chemical properties of the aerosol are captured into a single kappa-parameter (κ) while all other parameters are kept constant. For a more detailed assessment of the κ -Köhler equation, together with a comparison of other models that connect growth at sub- and supersaturation, see Rissler et al. (2010). Equation (5) can be derived from Eq. (1) by using the Zdanovskii, Stokes and Robinson (ZSR) assumption for multicomponent-water solutions at equilibrium, volume equivalent diameters (spherical particles) and applying a parametrization for the water activity of the solution (Petters and Kreidenweiss, 2007).

The Eq. (5) can be solved for κ by applying the saturation ratio (now $S < 1$), dry size, growth factor and temperature of the HTDMA measurement. Consequently, the d_{crit} corresponding to the obtained κ and a certain S can be determined from Eq. (5) by finding the dry size (d_{dry}) which produces the maximum value of the κ -Köhler curve (i.e. the point of activation) at the selected S . The critical dry diameters were determined for the supersaturations ($SS = S - 1$) used in the CCN measurements, i.e. $SS = 0.1, 0.2, 0.4, 0.6$ and 1.0 %. κ can only be calculated at the dry sizes used in the HTDMA, and each of these will typically yield a slightly different κ depending on the chemical composition of the aerosol at the measured sizes. With the above approach, converting κ to d_{crit} requires an application of κ to the entire range of d_{dry} . To minimize the effect of this, d_{crit} was always determined from the HTDMA dry size that was closest to d_{crit} . For consistency, the calculations were done using the surface

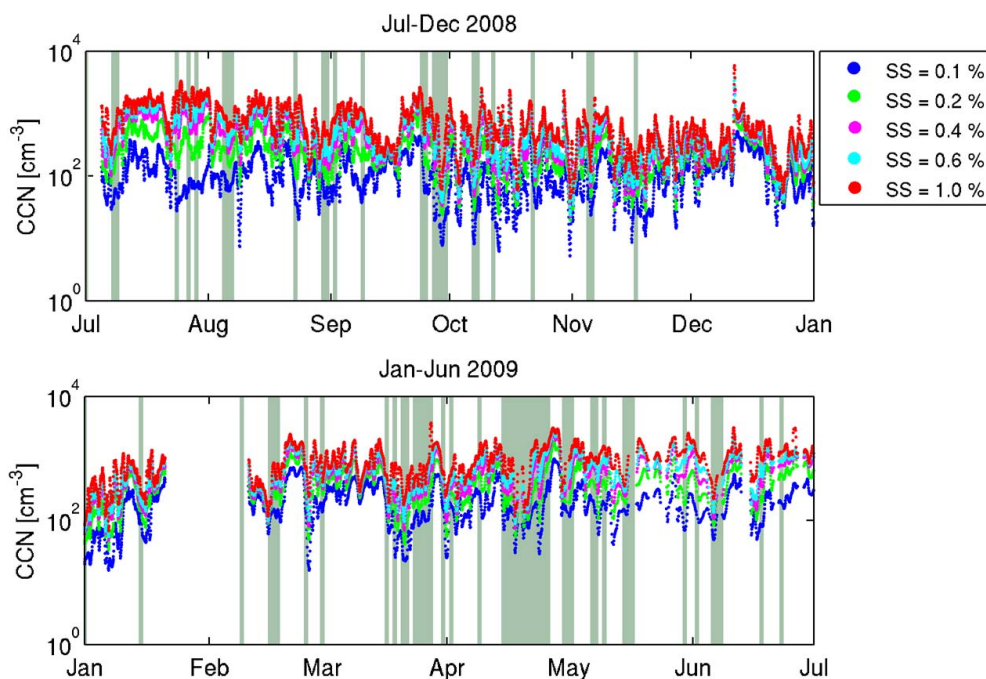


Fig. 1. Time series of CCN concentration at Hyytiälä SMEAR II station measured at five water supersaturations (SS): 0.1 % (blue), 0.2 % (green), 0.4 % (purple), 0.6 % (light blue), 1.0 % (red). The data points are 1 hour averages, which have been smoothed by taking a moving average with a 10 points window. Days with new particle formation (event days) are marked with a grey background.

tension of water, $\sigma_w = 0.072 \text{ J m}^{-2}$, as suggested by Petters and Kreidenweis (2007).

4 Results

4.1 The measured CCN concentrations

The time series of CCN concentrations for the analyzed one-year period is presented in Fig. 1. The CCN concentrations show a high variability from day to day, reflecting the variations in aerosol number concentration, size distribution and chemical composition. From this figure no clear seasonal pattern in the CCN concentration can be observed. Mostly the CCN concentrations seem to be lower on new particle formation event days (marked with a grey background) as compared to other days (this issue will be returned to later in Sect. 4.3.2.). When comparing the time series for different supersaturations with each other, there appears to be a larger difference between the different supersaturations in spring-summertime (May–August) than in wintertime.

The seasonal variation in CCN concentration becomes clearer when looking at monthly averages (Table 1 and Fig. 2). The CCN concentrations are the highest in the summertime and the lowest in the wintertime, with minimum values occurring in November–January. A comparison with the total particle concentration (CN, condensation nuclei) shows that the seasonal variation of the CCN concentration is not only due to variation in the CN concentration

(see Fig. 2a), but there are also differences in the size distribution and chemical composition, both of which contribute to the variation of the CCN concentration. This is reflected in the activated fraction (CCN/CN, Fig. 2b), which has somewhat different annual profile than the CCN concentrations. For instance, the minimum is shifted to October–November. The activated fraction at the highest supersaturations (0.4, 0.6 and 1.0 %) shows quite a large variation over the year, with a maximum in July. At those supersaturations, the activated CCN contain more (small) particles produced by nucleation events than at lower supersaturations.

We also examined the mean CCN concentration as a function of supersaturation, and determined parameters for the so called “CCN spectrum”, i.e. the parameterization

$$[\text{CCN}] = cSS^k, \quad (6)$$

where SS is supersaturation in percents. The values for the parameters c and k from this data set were $c = (1100 \pm 220) \text{ cm}^{-3}$ and $k = (0.6 \pm 0.2)$ (for mean $[\text{CCN}]$; for median $[\text{CCN}]$ $c = 990 \text{ cm}^{-3}$ and $k = 0.7$). These are within the range of values reported in literature for continental aerosol ($c = 600\text{--}3500 \text{ cm}^{-3}$ and $k = 0.4\text{--}0.9$; e.g. Seinfeld and Pandis, 1998). However, the parameterized CCN-concentration does not reproduce the measured CCN data and the mismatch is the worst at low supersaturations as the correlation coefficients are 0.34, 0.22, 0.16, 0.08 and 0.02 for $SS = 1, 0.6, 0.4, 0.2$ and 0.1% , respectively. Clearly the simple

Table 1. Monthly averages of CCN concentration, activated fraction (CCN/CN) and critical diameter, measured at SMEAR II station in Hyytiälä July 2008–June 2009. Superscripts *a* and *b* in CCN derived critical diameters represent averages calculated from all the available data (*a*) and from concurrent CCNC data with the HTDMA data (*b*), respectively. The data are for supersaturation of 0.4 % representing an average case in the range of measured supersaturations.

Month	CCN concentration [cm ⁻³]	Activated fraction	d _{crit} [nm] (CCNC) ^a	d _{crit} [nm] (CCNC) ^b	d _{crit} [nm] (HTDMA)
July 2008	804	0.42	81	79	88
August 2008	563	0.41	82	82	84
September 2008	514	0.36	83	90	88
October 2008	328	0.22	91	99	88
November 2008	261	0.21	99	90	78
December 2008	327	0.36	94	81	75
January 2009	336	0.31	82	78	81
February 2009	648	0.39	66	62	72
March 2009	567	0.35	62	61	78
April 2009	675	0.36	58	67	77
May 2009	744	0.33	68	66	81
June 2009	791	0.40	72	80	93

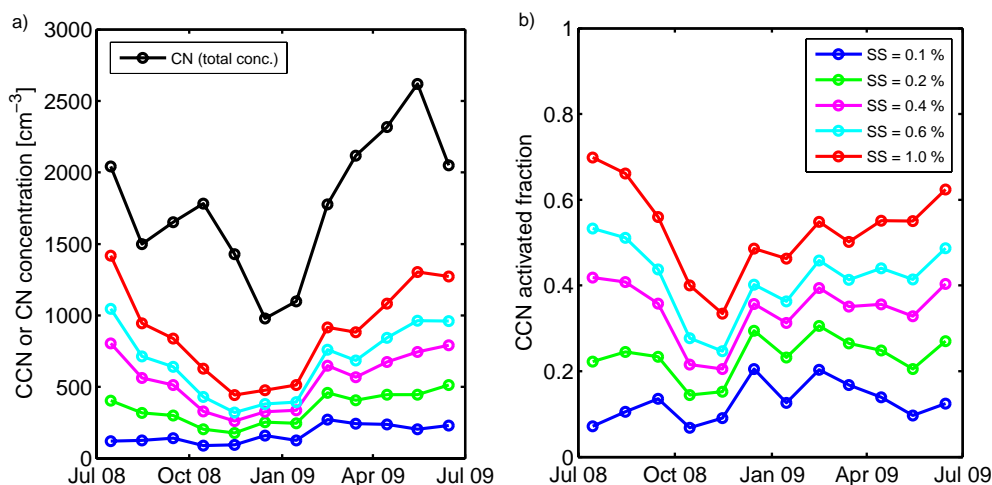


Fig. 2. (a) Monthly mean values of the CCN concentrations at different supersaturations and the total number concentration (CN), and (b) monthly means of the activated fraction (CCN/CN).

parameterization does not capture the temporal variability of the CCN population and should be applied with caution.

In January–February (21 January–10 February 2009) there was a break in the measurements due to some changes made for the measurement setup (a DMA was added in front of the CCNC to enable size-resolved measurements in the future), and therefore data for this period is missing (see Fig. 1). The concentrations stayed at similar level after the break, so we can assume that the observations before and after the break are comparable to each other.

4.2 The critical diameter for CCN activation

4.2.1 The critical diameter estimated from CCN and size distribution measurements

The critical diameter for cloud droplet activation was estimated from the CCN concentrations and particle size distributions measured with the DMPS (see Sect. 3.1). In principle, the variations in critical diameter reflect the variations in chemical composition of the aerosol: the more hygroscopic the aerosol, the smaller the critical diameter for activation.

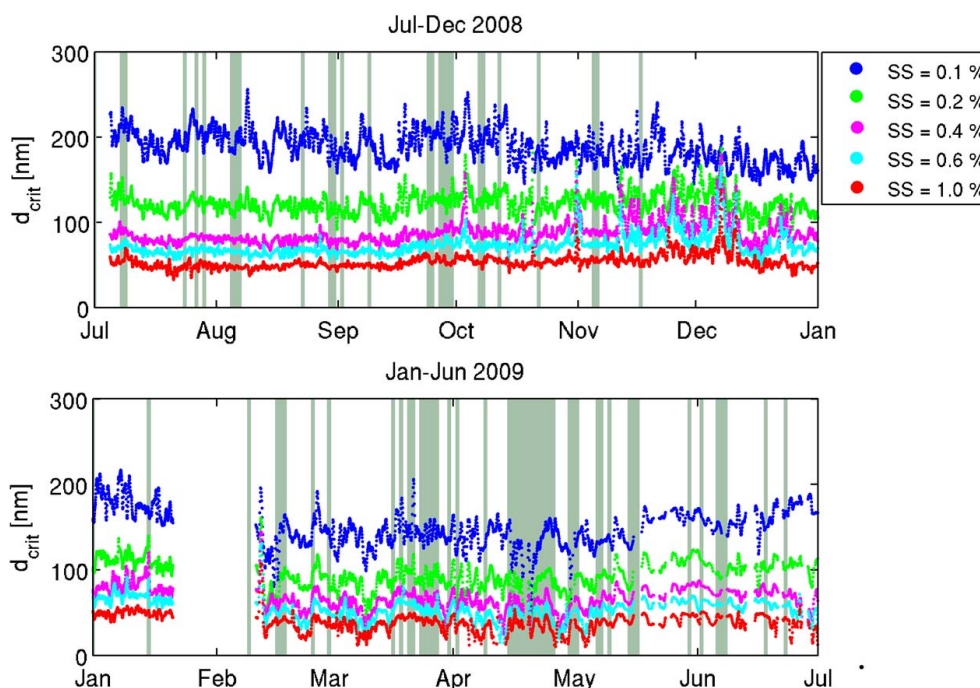


Fig. 3. Time evolution of critical diameter, estimated from CCNC data and particle size distribution data. Different colours correspond to five supersaturation (SS) levels: 0.1 % (blue), 0.2 % (green), 0.4 % (purple), 0.6 % (light blue), 1.0 % (red). The data points are 1 h averages which have been smoothed by taking a moving average with a 10 points window. Days with new particle formation (event days) are marked with a grey background.

Figure 3 shows the time series of the estimated critical diameters (Eq. 3) for the five supersaturations inside the CCN counter. The critical diameter varies from ~ 50 nm at a supersaturation of 1.0 % to ~ 180 nm at a supersaturation of 0.1 %. Day-to-day variability in the critical diameter is quite high.

Similarly as the CCN concentration, the critical diameter has a larger variation between different supersaturation levels in the summertime than in the wintertime. Especially d_{crit} for the lowest supersaturation ($SS = 0.1$ %) decreases in the winter (from December to March), and starts to increase again towards the summer.

Monthly mean values show that the critical diameter is the smallest in April and the largest in November for supersaturations > 0.1 % (Table 1 and Fig. 4). The maximum of d_{crit} in November corresponds to the minimum of CCN concentration and activated fraction (see also Fig. 2). For $SS = 0.1$ % the seasonal behaviour of d_{crit} is clearly different than for the other supersaturations.

When calculating the critical diameters from CCNC and DMPS data, a uniform chemical composition was assumed. It must be noted that this assumption may not be justified, if the aerosol population is highly externally mixed, having for example a big fraction of primary soot particles. However, with this method we can get an estimate for the activation diameter with a high time resolution, and investigate the general characteristics of its variation.

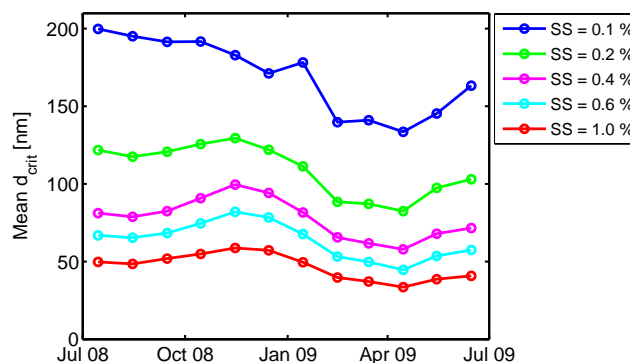


Fig. 4. Monthly mean values of critical diameter estimated from the CCN concentrations and size distribution measurements.

4.2.2 Comparison of d_{crit} from the CCN concentration and hygroscopicity measurements

For comparison, we determined the critical diameter values also from hygroscopicity measurements by applying κ -Köhler theory (Eq. 5). HTDMA data were available only for shorter periods between July 2008 and June 2009, and therefore we do not present the time series for it, but examine only the average values over a longer period. The monthly averages of the critical diameter at supersaturation of 0.4 % are listed in Table 1. The values from HTDMA data differed to

some extent from the values estimated from the CCN concentrations, but no systematic bias was observed. The seasonal behaviour was fairly similar in both critical diameter estimates, with the smallest values occurring in March–April. One reason for the differences between the two critical diameter estimates are the gaps in the HTDMA data, making the monthly averages not truly comparable with each other. Therefore, in the following we consider the one-year averages of the critical diameters.

Figure 5 compares the average critical diameters over the one-year data set estimated from the CCN concentrations and hygroscopic measurements. The critical diameter decreases linearly with supersaturation (with logarithmic scale in both axes), with a slope that is close to the theoretical value $-2/3$ given by the Köhler equation (e.g. Rissler et al., 2010). The values determined by these two methods are very close to each other. This gives confidence that our simple method to determine the critical diameter by integrating the size distribution seems to work reasonably well; and vice versa that the κ -Köhler model works for the Hyytiälä aerosol population. The variation in the critical diameters, as shown by the error bars, is slightly bigger for the CCNC data than for the HTDMA data.

Figure 5 also shows the data points for pure secondary organic aerosol (SOA) from the oxidation of α -pinene and trimethylbenzene (TMB) in laboratory measurements by Duplissy et al. (2008). The critical diameters in Hyytiälä are somewhat smaller than the laboratory measurements for the SOA, but clearly larger than those for pure ammonium sulphate. Aerosol particles at Hyytiälä measurement station, located in a pine forest in boreal forest region, are expected to have a high organic fraction, with α -pinene and other monoterpenes being the most important VOCs emitted by coniferous trees (e.g. Hakola et al., 2003; Tarvainen et al., 2005). Our measurements and the derived critical diameters indicate that the aerosol particles in Hyytiälä are not purely organic, but contains also more hygroscopic compounds, such as ammonium sulphate.

Besides the measured data points, Fig. 5 shows a line from the κ -Köhler equation (Eq. 7) using the average κ value determined from the HTDMA-data, $\kappa = 0.18$. Also the lines with the κ values reported earlier from the laboratory studies of monoterpene SOA ($\kappa = 0.04\ldots 0.24$, e.g. Engelhart et al., 2008) are plotted. Figure 5 shows that the κ -Köhler theory with $\kappa = 0.18$ is on average a good model for the cloud droplet activation in Hyytiälä.

Recently, Gunthe et al. (2009) reported a value $\kappa = 0.1$ for pure secondary organic aerosol in Amazonian tropical rainforest, and Dusek et al. (2010) found the same value for SOA at a rural Central-European site. The value $\kappa_{\text{org}} = 0.1$ is supported also by laboratory studies of SOA from α - and β -pinene (Petters and Kreidenweis, 2007; Duplissy et al., 2008; Jurányi et al., 2009). The average $\kappa = 0.18$ obtained in this study is somewhat higher, as expected, since the aerosol particles in Hyytiälä are not purely organic. The effective κ can

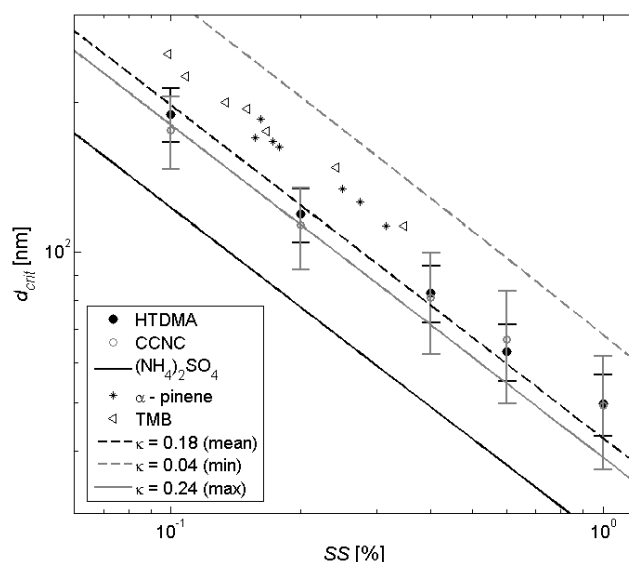


Fig. 5. Average critical diameter estimated from CCNC and HTDMA data as a function of water supersaturation. Error bars show the standard deviations over the one-year data set. Data from laboratory measurements by Duplissy et al. (2008) with α -pinene and trimethylbenzene (TMB) aerosol are plotted with markers (stars and triangles). Lines show theoretical values for pure ammonium sulphate particles (black solid line), and three different κ values. The $\kappa = 0.18$ was determined in this study, and $\kappa = 0.04$ and 0.24 span the range of κ values presented in the literature for organic (monoterpene) aerosol (Engelhart et al., 2008).

be calculated as a linear superposition from the aerosol constituents, for which κ values are known:

$$\kappa = f_{\text{org}} \kappa_{\text{org}} + f_{\text{inorg}} \kappa_{\text{inorg}}, \quad (7)$$

where κ_{org} and κ_{inorg} are κ -values of the organic and inorganic part and f_{org} and f_{inorg} their volume fractions (Gunthe et al., 2009). As shown by Raatikainen et al. (2010), the organic aerosol in Hyytiälä in spring/summer can be thought of as a mix of two oxidized organic aerosol constituents. Jimenez et al. (2009) converted the estimated growth factors of the two constituents to κ values of 0.2 and 0.0, respectively. Although Eq. (9) is a crude simplification as both κ values are likely to vary, the assumed $\kappa_{\text{org}} = 0.1$ is likely a good estimate for the average organic aerosol. Assuming $\kappa_{\text{inorg}} = 0.6$ for the inorganic part ($\kappa = 0.6$ for ammonium sulphate; Petters and Kreidenweis, 2007), we get the following fractions for organic and inorganic aerosol in Hyytiälä: $f_{\text{org}} = 84\%$ and $f_{\text{inorg}} = 16\%$. The organic fraction (84%) corresponds well to the estimates from growth rate analyses of newly formed particles, which predict the organic contribution to the average particle growth rate to be about 90% in Hyytiälä (e.g. Boy et al., 2005). On the other hand, the estimate is somewhat higher than the organic mass fraction of $\sim 60\text{--}70\%$ observed in aerosol mass spectrometer (AMS) studies in Hyytiälä (Jimenez et al.,

2009). Both the above-mentioned studies also focused on spring/summertime, and the organic fraction is likely to be lower in winter.

There are several reasons that could explain the difference between the organic fraction estimates. Firstly, the κ -parameter deals with volume fractions whereas the AMS measures mass. The density of organic material is often lower than that of inorganic compounds, making the organic mass fraction lower than the corresponding volume fraction. Secondly, there are also organic compounds with $\kappa_{\text{org}} < 0.1$ present in the Hyytiälä aerosol population as stated earlier, and on a yearly average these may be more common. Thirdly, hydrophobic black carbon gives a contribution (<20%; O'Dowd et al., 2000; Saarikoski et al., 2005; Carvalho et al., 2006) to the aerosol mass in Hyytiälä, and this is neither taken into account in Eq. (5) nor measured by the AMS. Finally, the estimated κ of 0.18 is an average over the 5 measured *SS* values. The three highest *SS* values give d_{crit} in the Aitken mode and the two lowest give d_{crit} in the accumulation mode. It is evident also from Fig. 5 that the hygroscopicity of the Aitken mode is lower than that of the accumulation mode. The Aitken mode particles are likely formed through gas-to-particle conversion and will be dominated by organics, whereas the accumulation mode particles can have experienced cloud processing, increasing the fraction of inorganic material. The AMS signal is dominated by mass, which means mostly accumulation mode, whereas the study of particle formation by Boy et al. (2005) concentrated on the smaller nucleation/Aitken mode particles. Our estimate, on the other hand, is an average of both Aitken and accumulation mode particles.

In this data set we did not observe a systematic difference between d_{crit} estimated from CCNC and HTDMA-measurements (although some non-systematic differences were seen, see Table 1), which would result from a non-linear hygroscopicity behaviour at RH close to 100 %, as reported by some studies (Petters and Kreidenweis, 2007; Wex et al., 2009; Good et al., 2010). In those studies, HTDMA data yielded bigger d_{crit} values (or smaller κ -values) than the CCN activity measurements. This discrepancy has been explained by the fact that when applying the κ -Köhler theory using hygroscopicity measurements, the CCN activation is “extrapolated” from the measurement in subsaturated conditions, at about RH = 90–98 %. The hygroscopicity may increase at relative humidities close to 100 %, which would cause a systematic bias to d_{crit} (and κ) values estimated from the hygroscopicity data. However, in this study this kind of effect was not seen; instead, at least on average, both methods gave similar results.

The good agreement between the HTDMA and CCN derived d_{crit} also suggests that the assumption of internally mixed particles did not strongly affect the results. Both methods assumed internally mixed particles, although the influence of an external mixture would not be identical in the two cases. The HTDMA growth factor distributions showed a

certain level of external mixture at the larger dry sizes (75 and 110 nm), and this was more pronounced in wintertime. Kammermann et al. (2010) performed a detailed analysis of different methods of predicting the CCN number from HTDMA and SMPS data, and found that ignoring the growth factor distribution and only using the average growth factor did not have a noticeable influence on the agreement. Additionally, as the growth factors were only measured at discrete dry sizes which were not equal to the d_{crit} , the external mixture may have been implied incorrectly, causing artefacts to the data. For these reasons, a simplified approach was used in this work.

CCN concentrations have been measured previously in Hyytiälä by Aalto and Kulmala (2000), but with a different instrument and measurement setup. In addition, the data analysis was performed in a different way concentrating mainly on estimating the soluble fraction from the CCNC data. Due to differences in the instrument and data analysis, the results of this and previous studies are not directly comparable with each other. Nevertheless, the critical diameter values obtained here are broadly consistent with the measurements by Aalto and Kulmala (2000), who reported an approximate activation diameter of 70 nm at supersaturation of 0.5 % for spring-summer 1998 in Hyytiälä.

4.3 Effect of new particle formation to CCN population

As mentioned earlier, new particle formation (NPF) is an important source of particles in the atmosphere, and some fraction of the formed particles reaches a size where they can act as CCN. In this section we study the effect of new particle formation on CCN properties in Hyytiälä by comparing the CCN concentrations, activated fractions and critical diameters on new particle formation days (event days) and on days with no particle formation (non-event days) classified according to Dal Maso et al. (2005). During the analysed one-year period (July 2008–June 2009), 75 new particle formation events were observed.

4.3.1 A case study of CCN activation on new particle formation days

An example of a new particle formation period with four consecutive particle formation events is shown in Fig. 6. New particle formation occurs typically around midday following the sunlight, and the growth of the nucleation mode particles continues until midnight and even during the next day. During the period presented in Fig. 6, both new particle formation events and changes in the background aerosol created contributed to the variations in the CCN concentration, activated fraction and critical diameter.

Each new particle formation event showed as a rapid increase in total particle number concentration (CN, black curve in Fig. 6). After NPF bursts, the CN concentration decreased due to coagulation. Meanwhile, the CCN

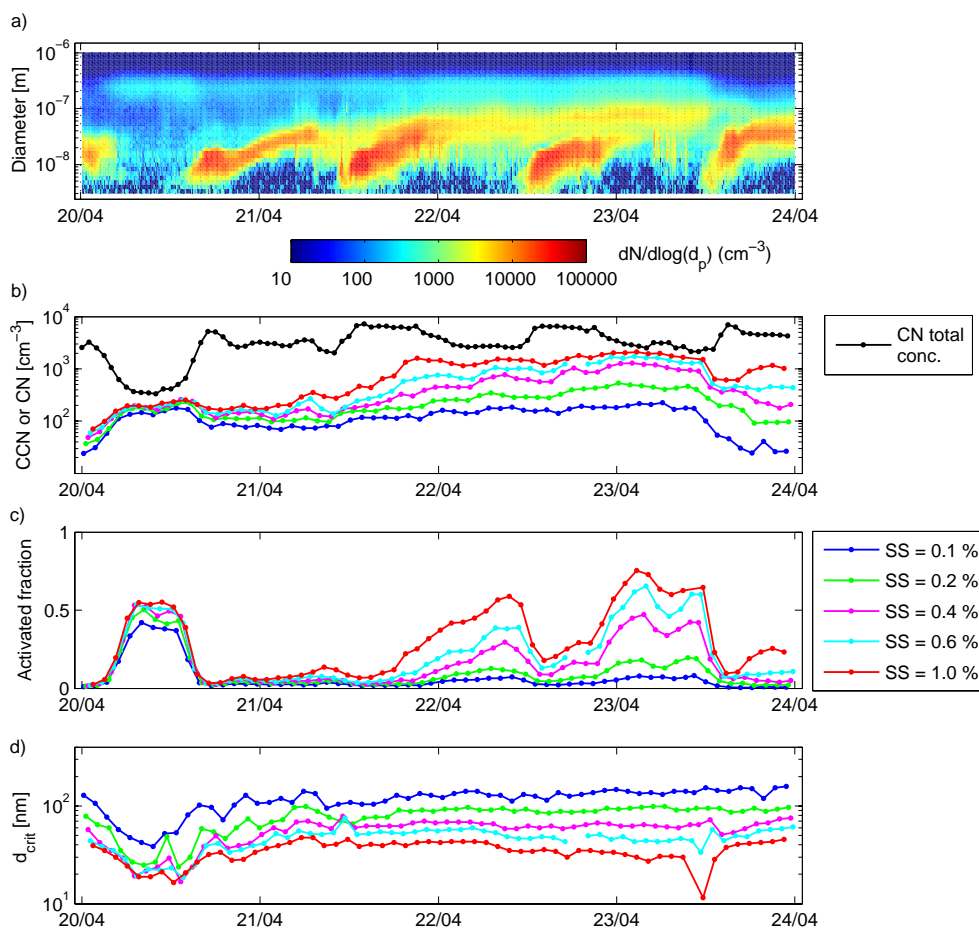


Fig. 6. Comparison of the time evolution of (a) particle size distributions, (b) cloud condensation nuclei (CCN) and total particle concentrations (CN), (c) activated fraction (CCN/CN), and (d) critical diameter (estimated from CCNC and size distribution measurements) on four consecutive new particle formation days in Hyytiälä (20 April–23 April 2009).

concentration showed less rapid changes and increased steadily during the first three NPF event days. Because the background aerosol number concentration was rather stable during this period, the increase in the CCN concentration can be attributed to the particles produced by the NPF events. The continuous increase in the CCN concentration was observed for all the supersaturations, but the increase was the greatest for $SS = 1.0\%$ (almost one order of magnitude from 100 to 1000 cm^{-3}), because at higher supersaturations bigger fractions of the nucleation mode particles activated. Before the fourth event on 23 April 2009, the background concentration dropped dramatically, which led to a rapid decrease in the CCN concentration at $SS = 0.1\text{--}0.6\%$, although the total number concentration increased because of high number of newly formed particles. The particles from the NPF event contribute to the increase of CCN concentration at the supersaturation of 1.0% (which includes particles above $\sim 40\text{ nm}$).

Because of quite large variations in the total particle number concentration, the activated fraction varied a lot even during one day. Typically, the activated fraction was very low

during a NPF event due to a high number of small particles produced. During the growth of the nucleation mode (especially for the two strong events on 21 April and 22 April), the activated fraction increased greatly to 0.5 and above (for $SS = 1.0\%$).

The effect of the background aerosol is seen specifically on the first measurement day (20.4.), when there was a clear change of air mass. The new air mass was very clean and had a very low particle number concentration. However, despite the large decrease in the CN, the CCN concentrations increased and the activated fraction rose to close to 0.5 during this period. This was partly caused by the appearance of accumulation mode particles at a size of a few hundred nm. The simultaneous dramatic decrease in d_{crit} to as low values as 20–40 nm is likely an artefact caused by an offset in either the CN or CCN concentrations that became more pronounced at the unusually low CN concentrations. Based on the observed wind direction (about 330°), this was a northern marine air mass, which are typically very clean.

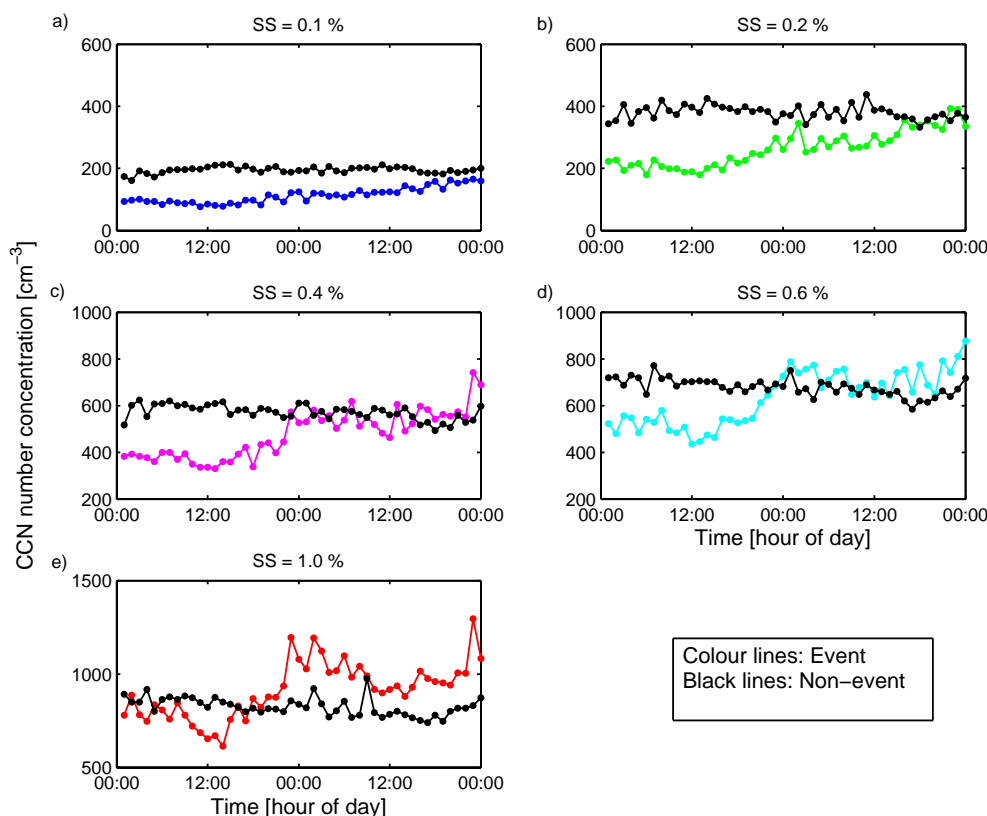


Fig. 7. Mean diurnal variation of CCN concentrations at different supersaturations (a–e) on two consecutive days, separated according to whether the first day was an event day (coloured markers) or a non-event day (black markers). The points are hourly averages over the one year data set.

The critical diameters stayed quite constant and were close to their mean values during the whole new particle formation period (21 April–24 April). A more careful inspection reveals that for the two highest supersaturations (0.6 and 1.0 %), the critical diameter decreased slowly and steadily from 21 April to 23 April, meaning that the particles around 30–60 nm became more hygroscopic in the course of time. This particle range contains a big fraction of recently nucleated particles. The increase in hygroscopicity is probably due to aging of the secondary organic aerosol, as reported by Jimenez et al. (2009). For the two lowest supersaturations (0.1 and 0.2 %), the critical diameter slowly increased from 21 April to 24 April. This particle size range, 90–180 nm, consists mainly of long-range transported particles and primary biogenic particles.

Measured increases in CCN concentrations associated with atmospheric new particle formation have been reported earlier by Kuwata et al. (2008) in Jeju Island, Korea, and by Wiedensohler et al. (2009) in Beijing, China. The results by Kuwata et al. (2008) were very similar to ours in that the increase in CCN was seen only at the highest supersaturations during the nucleation event day, with more apparent CCN increases observed in the following day. In Beijing, nucleated

particles grew more rapidly in size, such that increased CCN concentrations could be observed at all measured supersaturations already during the same day as nucleation occurred.

4.3.2 The diurnal profiles of CCN-properties on event and non-event days

To further investigate the effect of new particle formation on CCN-properties, we calculated mean diurnal profiles of CCN quantities on event and non-event days over the whole one-year data set. The diurnal variation of the CCN concentration for two consecutive days at five different supersaturation levels is presented in Fig. 7. Figures 8 and 9 show the profiles for activated fraction and critical diameter, respectively. A 48-h period was chosen, because particles produced by the NPF events continue to grow on the following day, and some fraction of them reach CCN-sizes only on the next day after the event as typical growth rates in Hyytiälä are $2\text{--}8\text{ nm h}^{-1}$ (e.g. Manninen et al., 2009). The classification of the 48 h period as an event period or a non-event period was done based on whether the first day (first 24 h in the figure) was an event or a non-event day, and paying no attention to the classification of the following day (last 24 h in the figure).

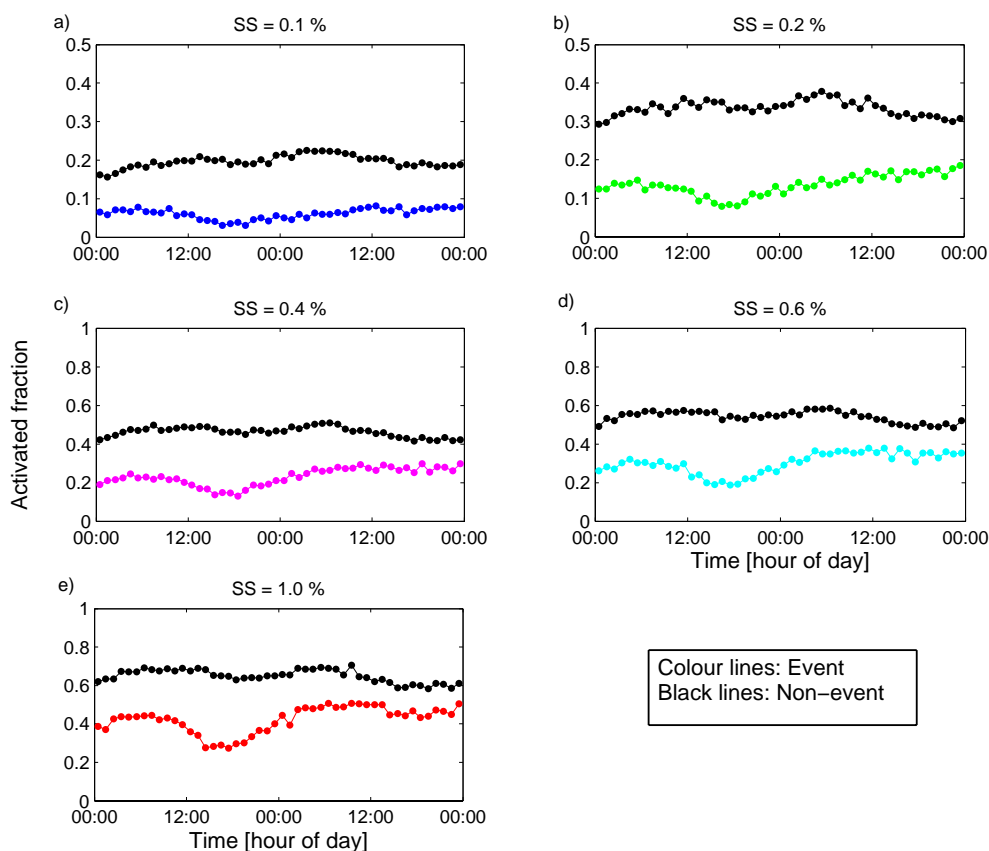


Fig. 8. Same as Fig. 7, but for the activated fraction (CCN/CN).

CCN concentration

Before noon the CCN concentrations were observed to be lower on the NPF event days than on the non-event days for all the supersaturations except for $SS = 1.0\%$ (see Fig. 7). This is explained by the fact that NPF events typically occur on days with low background aerosol concentration (leading to small coagulation and condensation sink) before the event (Hyvönen et al., 2005; Dal Maso et al., 2007), which also leads to a low number of particles activated as CCN.

On days without NPF, the diurnal profile of CCN concentration was relatively stable. On the other hand, on NPF days big variations were observed: the CCN concentration had a small minimum around noon, and after the NPF event (which occurs around noon) the concentrations increased towards the evening and stayed approximately at the same level on the following day. The increase in the CCN concentration was most pronounced and occurred first for the highest supersaturation ($SS = 1.0\%$), whereafter the increase could be seen consecutively at 0.6, 0.4 and 0.2 % supersaturation levels. The increases in the CCN concentrations on event-day evenings can be attributed to the particles produced by the NPF events. The increase was observed first at the highest supersaturation, corresponding to the activation of the particles

above ~ 50 nm, the size range which the nucleated particles reach in the afternoon. When the particles grow bigger, they are seen at smaller and smaller supersaturations corresponding to larger activation sizes. For the two lowest supersaturations (0.1 % and 0.2 %), the CCN concentration continued to increase on the day after the event, as it takes more time for particles to grow to the corresponding sizes (110–180 nm).

In percentages, the CCN concentration increased by about 70 % from an event-day midday to next day's midnight at the supersaturation of 1.0 %, and by 82, 70, 110 and 106 % at the supersaturation levels of 0.6, 0.4, 0.2 and 0.1 %, respectively (for absolute changes see Fig. 7). At the two lowest supersaturations (0.2 % and 0.1 %) the increase in CCN concentration was smaller in absolute numbers, but percentually the increase was greater (up to 110 % by the end of the two day period). Thus, NPF considerably increased CCN number concentrations on the following day, the increase being even a factor of two from the concentration level present before the event.

Activated fraction

The activated fraction (CCN/CN) was observed to be lower on event days than on non-event days (see Fig. 8). The activated fraction followed roughly a similar pattern as the

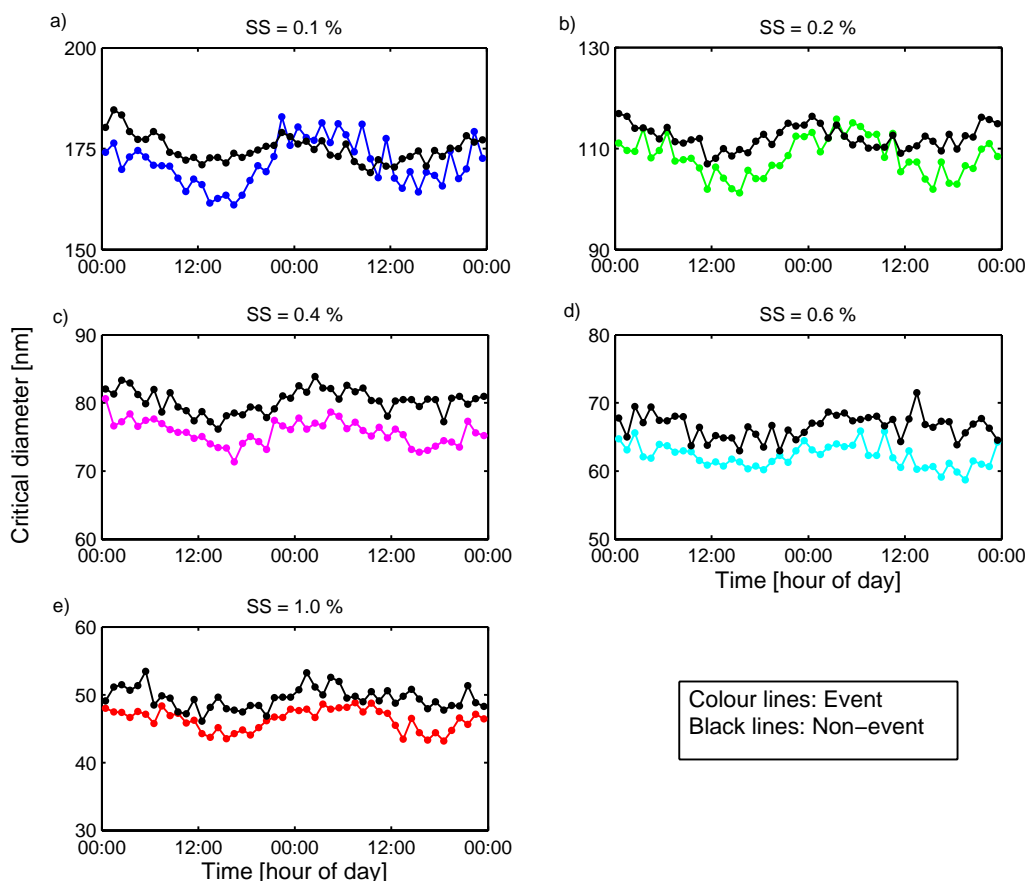


Fig. 9. Same as Fig. 7, but for the critical diameter determined from the CCNC and size distribution measurements.

CCN concentration (Fig. 7): the profiles were flat on non-event days, whereas on event days there was a minimum in the afternoon after which the activated fraction increased towards the next day. During the whole 48-h period, the activated fraction stayed lower on event days as compared with non-event days. This was mainly because the total particle number concentration (CN, condensation nuclei) was higher on event days than on non-event days (see Fig. A1 in Appendix). High CN concentrations make the activated fraction low on event days despite the substantial increases in CCN concentrations due to NPF (as shown in Fig. 7). At first sight it is surprising that also before noon the total particle concentration was higher on event days than on non-event days, as events should occur on days with low background aerosol concentration. However, for event occurrence it is the background aerosol surface area (i.e. the condensation and coagulation sinks) that is crucial, and for that the number of bigger particles has more influence (as seen also in Fig. 7, where the difference between event day and non-event day mornings disappears for the highest supersaturation). The high CN concentration in the morning of an event day is explained by the fact that during the “event-rich period” from spring to autumn, the NPF events often occurred on consecutive days.

This made the total particle number concentration high also in the morning of an event day, when the tail of the nucleated particle population was often observed.

In summary, the difference in the activated fraction between event and non-event days results mainly from the differences in the shape of the particle size distribution. Event days have more small particles and, before the event, fewer large particles. Also the differences in the particle chemical composition between event and non-event days may have some effect on the CCN concentrations, but the effect of size distribution is expected to dominate, as reported in earlier studies (e.g. Dusek et al., 2006; Quinn et al., 2008).

Critical diameter

The diurnal profile of the critical diameter on event and non-event days is presented in Fig. 9. On average, the critical diameter was somewhat lower on event days than on non-event days, but the difference was quite small, only a few nanometers. On both event and non-event days, there was a diurnal variation in the critical diameter with a minimum in the afternoon. The variation seemed to be more pronounced on event days, especially at lower supersaturations. In principle,

the variations in critical diameter should be related to the chemical composition (hygroscopicity or water activity) of the particles. The diurnal variation of d_{crit} was opposite to the variation of solar radiation, and it might be related to photo-chemistry (mainly through oxidation by OH radical). During daytime the oxidation products of VOCs condense on the particles and there might be chemical reactions on particle surfaces, which could change the hygroscopicity of the particles over the course of the day.

A relatively small difference in the value of d_{crit} between the event and non-event days indicates that there was no big difference in the particle chemical composition between the event and non-event days. However, it should be noted that in Fig. 9 the points were averaged over one year, during which the critical diameter showed some seasonal variation (see Fig. 4). This averaging may hide differences in the aerosol composition between the event and non-event days.

5 Conclusions

As a part of EUCAARI (Kulmala et al., 2009) activities, the CCN properties at Hyytiälä SMEAR II station were investigated by analyzing one year data of CCN concentrations and hygroscopicity measurements. The critical diameters for cloud droplet activation were estimated using two methods: from the CCN concentrations by integrating the particle size distribution, and from the hygroscopic growth factors by applying the κ -Köhler theory. Both methods gave very similar results. No systematic difference between the values from hygroscopicity and CCN measurements was observed, as reported in some earlier studies (e.g. Petters and Kreidenweis, 2007). This means that our method to calculate the critical diameter by simply integrating the size distribution, without any assumption of the chemical composition, seems to work reasonably well in Hyytiälä conditions, at least when applied to long-term averages. The critical diameter values obtained here were broadly consistent with the earlier measurements by Aalto and Kulmala (2000).

The CCN number concentrations showed a large seasonal variation, with the concentrations being more than a factor of two higher in summer than in winter. The critical diameter had a maximum in November and a minimum in April. The seasonal variation was similar for supersaturations 0.2–1.0 %, but clearly different for the supersaturation of 0.1 %. This could be related to the fact that the CCN measurements at supersaturations 0.2–1.0 % (corresponding to critical diameters from 120 to 50 nm) are affected by new particle formation, whereas the measurements at the supersaturation of 0.1 % (critical diameter \sim 180 nm) reflect mainly long-range-transported background aerosol particles.

New particle formation was observed to increase the CCN concentrations in the evening of a new particle formation day. The CCN concentrations increased on average by 70–110 % from the event-day midday to the next-day midnight, depending on the supersaturation level. The activated fraction was

smaller on event days than on non-event days, and showed only a small increase towards the evening on event days due to a high number of small particles produced by nucleation. In case of the critical diameter, no significant difference between the event and non-event days was observed. On both the event and non-event days, the critical diameter had a small sinusoidal diurnal variation with a minimum in the afternoon related probably to the OH-driven chemistry.

Comparison with the laboratory measurements by Duplissy et al. (2008) showed that the critical diameter in Hyytiälä was somewhat smaller than that for pure secondary organic aerosol from α -pinene or trimethylbenzene. The average value for κ -parameter, determined from the hygroscopicity measurements, was 0.18. Both the critical diameters and the value of κ indicate that the aerosol in Hyytiälä was slightly more hygroscopic than pure secondary organic aerosol.

Our value for the κ -parameter corresponds well to the values reported earlier. The value of $\kappa = 0.15$ has been reported by Engelhart et al. (2008) for monoterpene SOA produced in a smog chamber and by Gunthe et al. (2009) for a measurement campaign in Amazonian rainforest. A value of $\kappa_{\text{org}} = 0.1$ for pure organic aerosol has been proposed (Gunthe et al., 2009; Dusek et al., 2010). The value of $\kappa = 0.18$ in Hyytiälä indicates that aerosol is mostly organic and that also includes more hygroscopic salts such as ammonium sulphate. By assuming $\kappa_{\text{org}} = 0.1$ for organic part and $\kappa_{\text{inorg}} = 0.6$ for inorganic part, we estimated the average organic fraction to be 84 % and inorganic fraction 16 % for the aerosol in Hyytiälä. This organic fraction is close to the organic contribution of \sim 90 % estimated from the particle growth rates (Boy et al., 2005), but somewhat higher than the value of \sim 70 % obtained from aerosol mass spectrometer studies in Hyytiälä (Jimenez et al., 2009).

Our measurements give several implications for the modelling of CCN activation in boreal forest areas in global models. The seasonal variation in critical diameter is significant and should be taken into account. New particle formation has a significant effect on CCN number concentrations and should also be taken into account for an accurate prediction of CCN concentrations. The κ -Köhler theory with $\kappa = 0.18$ and a typical growth factor for secondary organic aerosol was attested to be a good model for CCN activation in Hyytiälä boreal forest conditions.

In the future, a more detailed analysis applying data of the particle chemical composition is needed to better understand the role of chemical composition on CCN activation in boreal forest conditions. The first step is already presented in Cerully et al. (2011) for spring 2007 data. Analyses of continuous multi-year and multi-site datasets, as in Asmi et al. (2011) for the aerosol number concentrations, are needed to more reliably distinguish the seasonal patterns, inter-annual variation and spatial variability of the CCN properties.

Appendix A

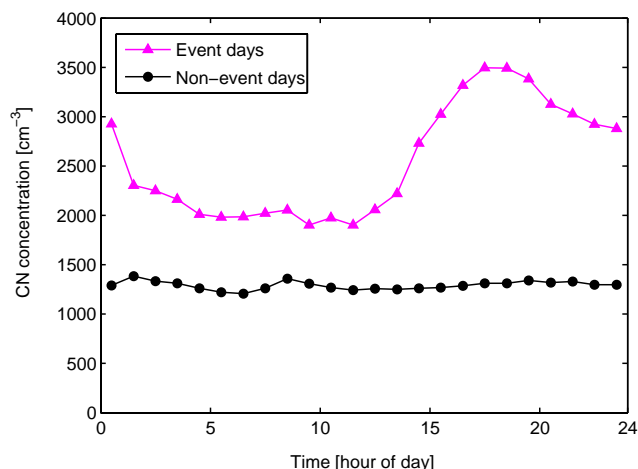


Fig. A1. Mean total particle number concentration (CN, diameter range 3–1000 nm) on event and non-event days at Hyttiälä SMEAR II station.

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